TITLE OF THE INVENTION

FUEL CELL

BACKGROUND OF THE INVENTION

(Field of the Invention)

5   This invention relates to fuel cells, particularly to polymer electrolyte fuel cells.

(Related Art)

A polymer electrolyte fuel cell (hereinafter called PEFC) that uses a polymer electrolyte has

10   merits of high output, long service life, little deterioration by starting and stopping, low operating temperature (approx. 70 to 80°C) and needs no precise differential pressure control, etc. Therefore, it has a very wide range of applications such as power

15   supplies for electric automobiles, distributed power supplies for industrial or business use and home use and so on.

A unit fuel cell of the PEFC comprises

a membrane-electrode assembly (hereinafter called

20   MEA) having a proton exchange membrane (hereinafter called PEM), which is proton-conductive sandwiched between porous electrodes coated with platinum or alloy catalyst such as platinum-ruthenium alloy and

a unit cell separator having gas flow channels

25   which supply hydrogen gas to the anode and air

(oxygen) to the cathode, respectively.

The PEM must be wet to a certain level to let protons move. To keep the PEM wet, a humidified fuel gas is usually fed to the anode or cathode. Various mechanisms have been proposed as apparatus to humidify fuel gases (for example by patent documents 1 to 7 shown below).

A humidifying mechanism using only a water permeable membrane has a problem that hydrogen gas bubbles passing through the water permeable membrane gather in the water supply side and prevent water from passing through the membrane. To solve this problem, a method has been disclosed in patent document 4, which comprises providing a platinum catalyst layer in the water supply side of the membrane, causing the hydrogen gas passing through the membrane to react with the oxygen gas dissolved in the supplied water, and thus eliminating hydrogen bubbles.

Patent document 1: Japanese Application Patent Laid-Open Publication No. 06-124722 (Page 3, FIG... 4)

Patent document 2: Japanese Application Patent Laid-Open Publication No. 07-65845 (Page 2, FIG... 9)

Patent document 3: Japanese Application Patent Laid-Open Publication No. 08-138704 (Page 3, FIG... 2)

Patent document 4: Japanese Application Patent

Laid-Open Publication No. 08-138705 (Page 2, FIG... 4)

Patent document 5: Japanese Application Patent Laid-Open Publication No. 08-250130 (Page 4, FIG... 7)

Patent document 6: Japanese Application Patent Laid-Open Publication No. 09-92308 (Page 5-6, FIG... 1)

Patent document 7: Japanese Application Patent Laid-Open Publication No. 11-185777 (Page 3, FIG... 5)

However, a humidifier using a conventional water permeable membrane has a problem that the pressure difference between the fuel gas and the cooling water that passes through the water permeable membrane will make the membrane project towards the low-pressure side during power generation. This membrane projection will narrow the fuel gas flow channels and reduces the flows of the fuel gas and the cooling water.

As a result, auxiliary devices that supply the cooling water and the fuel gas consume more power to supply them against the pressure loss. This reduces the efficiency of the fuel cell system including the auxiliary machines and the fuel cell.

SUMMARY OF THE INVENTION

The PEFC that is an embodiment of this invention basically includes a plurality of unit cells each of

which comprises a membrane electrode assembly (MEA) and unit cell separators which sandwich the MEA. These unit cells and cooling water separators are connected in series (into a laminated unit cell structure) to

5 generate enough electric power. The MEA comprises an anode having a catalyst and being porous, a solid polymer electrolyte having proton conductivity and a cathode having a catalyst and being porous, the members being laminated.

10 The PEFC of the invention is provided with a humidifier having a porous material, wherein cooling water is supplied to the membrane from part of its surface opposite to the water supplying surface of the porous member and/or from the outer periphery of said

15 porous member. The cooling water is supplied to humidify the fuel gas from the water supplying surface towards the gas flow channels.

BRIEF DESCRIPTION OF THE DRAWINGS

20 Fig. 1a shows a cross-sectional view of a PEFC of this invention, equipped with a humidifier.

Fig. 1b is an enlarged sectional view of the encircled part with a dotted circle in Fig... 1a.

Fig. 2 shows a cross-sectional view of a

25 humidifier of this invention and its vicinity.

Fig. 3 shows a water retaining layer holder used in this invention.

Fig. 4 shows a front view of the unit cell separator on anode side used in this invention.

5   Fog. 5 shows a cross-sectional view of a humidifier using a porous filter and its vicinity.

Fig. 6 shows a schematic diagram of a power generation system using the fuel cell assembly of an embodiment of this invention.

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DETAILED DESCRIPTION OF THE INVENTION

(Description of the Preferred Embodiments)

This invention will be described in further detail by way of embodiments

15   (Embodiment 1)

Fig. 1 shows a schematic diagram of the PEFC. The PEFC 100 comprises unit cells 101 each of which comprises MEA shown in Fig.1a and having a positive electrode 103a on one side thereof and a negative

20   electrode 103b on the other side, two gas diffusion layers 106 in contact with these electrodes (103a and 103b), and two unit cell separators 104 which sandwich the gas diffusion layers from the outside thereof, and cooling water separators 107 with one surface grooved

25   to flow cooling water which sandwich every two sets of

the above unit cells in series. This structure is called a unit cell assembly 119.

The gas diffusion layer is provided to assure water drainage ability, gas diffusion ability, and current collection ability.

A gasket 105 is inserted into a space between two unit cell separators 104 to prevent leakage of the fuel gas.

There are two kinds of fuel gases used in the PEFC: anode gas that is supplied to the positive electrodes and cathode gas that is supplied to the negative electrodes. Hydrogen gases obtained by modifying methane and gases that contain hydrogen are used as anode gases. Gases such as air that contain oxygen are used as cathode gases.

Generally used as PEM 102 is a membrane of fluoropolymer whose part of fluorine atoms in the pendant alkyl chains are substituted with sulphonic groups. Any polymer can be used as long as it has a function of moving hydrogen ions (protons). One of such polymer membranes is, for example, a polytetrafluoroethylene membrane prepared by substituting parts of fluorine atoms in tetrafluoroethylene as repeating units with alkyl chains having 2 to 5 units of $-CF_2-$ and/or $-CF_2(CF_3)-$,

etc., the fluorine atoms in the alkyl chains being

further substituted with sulfonic groups ($-SO_3H$).

The positive electrodes 103a and the negative

electrodes 103b are molded from a mixture of catalyst

5   (platinum or alloy of different kinds of elements such

as platinum and ruthenium), carbon powder, and binder.

At the anode 103a, the oxidation of hydrogen

(Formula 1) is going on. At the cathode 103b, the

reduction of oxygen (Formula 2) is going on. The

10   hydrogen ions (proton) produced by the oxidation of

hydrogen at the anode 103a travel to the PEM 102. The

PEM receives the hydrogen ions and emits electrons.

The electrons flow through an external load towards

the cathode and work to combine the hydrogen ions and

15   oxygen there into water.

$$H_2 \rightarrow 2H^+ + 2e^-$$ (Formula 1)

$$2H^+ + 1/2O_2 + 2e^- \rightarrow H_2O$$ (Formula 2)
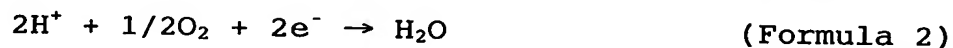
These reactions are accompanied by diffusion of

gases and movement of hydrogen ions. These movements

20   of substances generate resistances and cause a voltage

drop of the PEFC. To suppress this voltage drop, the

electrodes and the PEM must be thinner (to several

hundred microns). Therefore, the MEA comprising a PEM

sandwiched by electrodes is used.

25   Cooling water is supplied to the cooling-water

separator 107 from a cooling water pump 615 (Fig. 6)
that is placed outside the PEFC 100. This cooling
water deprives the PEFC of the generated heat, and
becomes warm. This warm water can be used for home use.

5   Further the PEM contains hydrogen ions that can
move in the membrane but their movement is very slow
when the membrane is dry. When the PEM is wet, water
carries the hydrogen ions with it and consequently,
the hydrogen ions move faster. A method of humidifying
10   fuel gases is employed to humidify the PEM. The water
to humidify fuel gases is called "humidifying water."
The humidifying water is part of water supplied by the
cooling water pump 615 (Fig. 6) through the cooling
water port 111 on the end plate 109.

15   The gas for the anode 103a is supplied through the
anode gas supply port 110. Usually, the humidifier 108
is provided next to the anode gas flow channels to
humidify the gas. The gas for the cathode 103b is
supplied through the cathode gas supply port 112.

20   A fuel cell assembly is built up by placing unit
cells 101 in series, connecting current-collecting
plates with output terminals (hereinafter called
collectors) 113 and 114 to which an external load is
connected to take out electric power to both ends of
25   the serial set of unit cells, placing an insulating

plate between each collector (113 or 114) and the end
plate 109 to electrically insulate the end plates from
collectors, placing unit cells 101, cooling water
separators 107, the humidifier 108, and collectors 113

5   and 114 in parallel, and fixing them together with
bolts 116, conical spring washers 117, and nuts 118.

Fig. 2 shows a magnified cross-sectional view of
the humidifier 108 of Fig. 1 and its vicinity to show
the detailed inside structure of the humidifier.

10   The humidifier 108 comprises a water permeable
membrane 201 that can transfer water, a water
retaining layer 203, and a holder 206 for holding the
layer 203.

The water retaining layer 203 is a porous material

15   that stores (holds) water in it and discharges water
to the surrounding according to the humidity
transition in the environment of the water supplying
surface and its vicinity.

The cooling water that recovers heat generated in

20   the unit cells 101 is supplied to the cooling water
flow channel 204 that passes through the humidifier
108 via the cooling water port 111 of Fig. 1 by the
cooling water pump 615 (Fig. 6) provided outside the
PEFC 100. Part of this cooling water is diverted as

25   humidifying water to humidify the anode gas from the

humidifying water inlet 202 into the water retaining
layer 203 and retained in micro-pores of the water
retaining layer 203. This embodiment carries out
retaining of the humidifying water by the capillary

5   action. When the PEFC 100 works, part of the water
held in the water retaining layer 203 is taken by the
anode gas that flows near the water supplying surface
207 of the water retaining layer 203 against the
capillary force and humidifies the anode gas. The

10   humidified anode gas moves into the unit cell 101
through the anode gas flow channel 205 and humidifies
the PEM 102. The wet PEM 102 facilitates the movement
of hydrogen ions in the PEM 102.

When the PEFC 100 stops, the anode gas flow stops

15   and the anode gas flow near the water supplying
surface 207 becomes less than that when the PEFC 100
is working. Accordingly, the humidifying water held in
the water retaining layer 203 remains held in micro-
pores of the water retaining layer 203 by the

20   capillary force. This can prevent the anode gas from
being humidified too much and reduce the humidity of
the anode gas. In other words, only when the PEFC is
working, the anode gas can be humidified.

This can also prevent the water retaining layer

25   203 from projecting towards the gas flow channel,

which always occurs when the cooling water is supplied
from part of a surface opposite to the water supplying
surface of the water retaining layer 203 and/or from
the outer edge of the water retaining layer 203.

5   In Fig. 2, the surface 207 is the water supplying
surface of the water retaining layer 203 and the
surface 208 is the surface opposite to the water
supplying surface. The portion 209 is the outer edge
of the water retaining layer 203. It includes all

10   surfaces of the water retaining layer 203 except the
water supplying surface 207 and the surface 208
opposite to the water supplying surface.

       There are various ways to supply water to the
water retaining layer: water supply by a pump or water

15   supply from a water tank by the gravitational force.
However, a preferable water supply method is making
part of the water retaining layer in contact with the
cooling water of the PEFC as in the humidifying water
inlet 202 and causing part of the cooling water to

20   osmose into the water retaining layer by the capillary
action. Particularly, this method is more preferable
because the heat generated by the PEFC can be used for
supply of the humidifying water.

       Materials fit for the water retaining layer can be

25   hydrophilic polymer materials that can hold enough

water, for example, hydrophilic polymer material, carbonaceous porous material, or compound thereof.

Typical hydrophilic polymer materials are of sponge-like sheets such as polypropylene non-woven cloth and polyethylene-polypropylene non-woven cloth. These materials are made hydrophilic by sulfonation. The proton substitution type sulfonation is preferable. If the sulfonation of substitution type of the other ion such as alkali metal (Li, Na, K, etc.) and alkali earth metal (Ca, etc.) is made, these hydrated metal ions are dissolved in water and carried by the anode gas to the PEM 102. The alkali metal ions react with hydrogen ions in the PEM 102 and the resulting product increases the resistance of the PEM 102. Consequently, this reduces the power generating performance of the PEM 102.

The average micro-pore diameter (R) of the porous material for the water retaining layer 203 can be expressed by

$$R = \gamma\cos\theta/\Delta P$$

wherein

ΔP is a difference between the pressure of cooling water supplied by the cooling water pump 612 (Fig. 2) or water to cool the PECF and the pressure of anode gas.

θ is a contact angle of water on the micro-pore surface.

γ is a surface tension of water.

In the above expression, for example, let's assume
5   that the porous material is hydrophilic and completely wettable with water. In this case, the contact angle (θ) can be approximate to zero. Judging from the necessity to reduce the power consumption of the cooling water pump 615 (Fig. 6), the pressure of the
10   cooling water supplied to the PEFC should preferably be in the range of 1 to 10 KPa. When the water pressure is 1 KPa, the average micro-pore radius is 130 microns (that is, the average micro-pore diameter is 260 microns). When the water pressure is 10 KPa,
15   the average micro-pore radius is 13 microns (that is, the average micro-pore diameter is 26 microns).

As the result, it is preferable that the water retaining layer 203 is a hydrophilic porous material that can hold water quickly and that the average
20   micro-pore diameter is in the range of 10 to 300 microns. In this case, this micro-pore size is a maximum micro-pore diameter and preferably causes a pressure higher than the cooling water pressure in the capillaries. In other words, the micro-pore diameter R
25   should preferably be equal to or smaller than the

function R(X) of the cooling water pressure ΔP.
Particularly, it is experimentally known that, when
the micro-pore diameter is in the range of 30 to 200
microns, the humidifier 108 can reject excessive water
and the almost saturated humidity can be obtained.

The thickness of the water retaining layer should
preferably be in the range of 50 to 300 microns. We
inventors experimentally found that it is possible to
reduce the quantity of supply of the humidifying water
by compressing the humidifying water inlet 202 so that
the thickness of the humidifying water inlet 202 may
be about 1/2 to 3/4 of the thickness of the water
retaining layer and that the gas can be humidified to
required degrees according to the flow rate of the
fuel gas.

The compression of the humidifying water inlet 202
is dependent upon the flow rate of a gas to be
humidified or the flow rate of water used for
humidification of the gas. The quantity of compression
is reduced to increase the flow rate of water.

This embodiment uses a hydrophilic polyethylene-
polypropylene non-woven cloth of 180 microns thick and
30 microns in average micro-pore diameter as the water
retaining layer 203. The surface of the non-woven
cloth is plasma-processed to have oxygen groups (=O,

-OH, etc.) to make it hydrophilic. With this, the water retaining layer becomes hydrophilic.

Although this embodiment employs a plasma method to make the water retaining layer hydrophilic, the

5 similar effect can be obtained by substituting part or all hydrogen atoms of polyethylene by fluorine atoms and substituting these fluorine atoms by sulfonic groups.

We can monitor the shapes of micro-pores of the

10 water retaining layer 203 by a scanning electron microscope. Generally, most micro-pores of the water retaining layer have indefinite shapes.

The micro-pore diameters of the water retaining layer 203 can be determined by taking microscopic

15 images of the surface of the water retaining layer 203 by a scanning electron microscope, calculating the area of each micro-pore by image processing of the microscopic images, obtaining a circle having the same area, and calculating its diameter. The average micro-

20 pore diameter is the average of the above micro-pore diameters. However, as the scanning electron microscope can hardly monitor surfaces of insulating materials, the other method can be employed to determine the micro-pore diameters of insulating

25 materials. In other words, the cross-sectional area of

each micro-pore of an insulating material can be estimated by filling the micro-pores with a conductive resin by pressure injection and observing the surface of the material by the scanning electron microscope.

5   The average diameter can be obtained by taking a microscopic image of the center area 308 (the hatched area in Fig. 3) of the water supplying surface 207 of the water retaining layer which is in contact with the fuel gas by a scanning electron microscope, measuring

10   the micro-pore size distribution in the microscopic image (photo), and calculating the average of the micro-pore diameters. The viewing field of the scanning electron microscope for measurement of a micro-pore size distribution is dependent upon the

15   shape of the fuel gas flow channel. It should be an area at which the fuel gas is actually humidified by the water retaining layer 203 and preferably be an area at which the fuel gas is humidified most easily. In other words, it should be an area that is greatest

20   in the gas-contact time and area. In a certain shape of the fuel gas flow channel, the area should be the center of the water supplying area 207 or its vicinity where the fuel gas is actually humidified by the water retaining layer 203.

25   Various hydrophilic polymer membranes can be used

as the water permeable membrane 201. They can be proton type ion exchange resin membranes, hydrophilic olefin membranes, sulfonated polystyrene membranes, and styrene sulfonic acid membranes. For example, the

5   PEM 102 is used as a polymer membrane which is prepared by substituting parts of fluorine atoms in tetrafluoroethylene repeating units of polytetrafluoroethylene polymer with alkyl chains having 2 to 5 of $-CF_2-$ and/or $-CF_2(CF_3)-$, etc., the

10 fluorine atoms being substituted with sulfonic groups $(-SO_3H)$.

As the heat resisting properties, the water permeable membrane must have at least higher melting and softening points than the operating temperature of

15 the PEFC. As the PEFC 100 uses water to cool the cell, the water permeable membrane should preferably has a melting point of 100°C or higher.

This embodiment uses, as the water permeable membrane 201, a polymer membrane prepared by

20 substituting parts of fluorine atoms in polytetrafluoroethylene polymer with alkyl chains having 2 to 5 $-CF_2-$ and/or $-CF_2(CF_3)-$, etc., the fluorine atoms being substituted with sulfonic groups $(-SO_3H)$.

25 The thickness of the water permeable membrane 201

in this embodiment affects the humidity of the fuel gas. As the thickness of the membrane in which water moves becomes smaller, the humidification rate increases. In this range, the water and the gas must

5   be separated from each other. Therefore, the thickness of the membrane must be in the range of 10 to 100 microns and preferably in the range of 20 to 50 microns. The reason for the low membrane thickness limit of 10 microns is that the thinner thickness may

10   not keep the strength of the membrane. Similarly, the reason for the high membrane thickness limit of 100 microns is that the greater thickness may increase the travel of water and reduce the humidification rate.

As the result, this embodiment employs the water

15   permeable membrane 201 of 30 microns thick.

Further, the water permeable membrane 201 should preferably be formed on the water supplying surface 207 of the water retaining layer 203 by a method such as bonding, joining, and contact. One bonding example

20   is applying a small amount of monomer that is the raw material of the water permeable membrane 201 or ion exchange resin as the adhesive to the surface of the water permeable membrane 201 and attaching the water permeable membrane to the water retaining layer 203.

25   This adhesive can be of any material as long as it

does not prevent water from moving to the water permeable membrane 201 from the water retaining layer 203. It is also possible to join the water permeable membrane 201 to the surface of the water retaining

5　　　layer 203 by compressing, heating, or the other joining means.

In this embodiment, the water permeable membrane 201 is bonded to the water retaining layer 203 with a small amount of monomer of the polymer membrane as an

10　　　adhesive therebetween.

The surface of the water permeable membrane 201 should be finely jagged to increase the specific surface area of the wet membrane with which the anode gas is in contact and to increase the humidification

15　　　rate. This can make the whole humidifier 108 smaller and also reduce the dimensions of the whole PEFC 100. The water permeable membrane 201 can have any patterned intended surface such as pleated surface and sponge-like surface as long as it is finely jagged.

20　　　Further, it is possible to change the humidification rate of the anode gas according to the flow rate of the fuel gas by changing the micro-pore sizes of the water permeable membrane 201. In other words, when the micro-pore size of the water permeable

25　　　membrane 201 becomes smaller, the humidification rate

of the anode gas decreases. Contrarily, when the micro-pore size becomes greater, the humidification rate of the anode gas increases.

5   This embodiment applied cooling water of 70°C to the water permeable membrane 201 of 0.03 micron in average micro-pore diameter and porosity of 0.7. Under this condition, the water permeable membrane 201 can humidify the anode gas to the saturated vapor pressure at 65°C. Here, the porosity is defined as the result

10 of "1 minus the quotient of division of apparent density by true density."

The water retaining layer 203 and the water permeable membrane 201 are held by water retaining layer holder 206 made of graphite. Generally, the

15 holder 206 should be as big as the separator of the fuel cell and the area of the water retaining layer 203 is limited. Therefore, if one water retaining layer is not enough for humidification, two or more water retaining layers can be used to increase the

20 humidification rate.

The PEFC 100 is generally used with the separator having fuel gas flow channels placed upright. Similarly, the humidifier 108 and the water permeable membrane 201 are also held vertically in the PEFC. As

25 the result, the humidifying water taken into the water

permeable membrane 201 goes down by gravitation and causes the lower part of the water permeable membrane 201 to swell. This may block the gas flow channels adjacent to the water permeable membrane, reduces the

5   humidification rate, and increases a gas pressure loss. To solve these problems, it is possible to provide a water-repellent porous material (not shown in the Figures) on the anode gas channel side of the water permeable membrane 201. This can prevent blockage of

10 anode gas flow channels and reduction of humidification rate also in the lower part of the humidifier 108. The reason for "water-repellent" is that the hydrophilic material condenses the humidifying water in its micro-pores before the

15 humidifying water evaporates and this deteriorates the gas humidification.

Carbon paper, carbon cloth, metal mesh, porous metal material and so on are available as the porous materials.

20 Fig. 3 shows a right side view of the water retaining layer holder 206. The humidifying water inlet 202 is a water regulating part that prevents excessive water from entering the water retaining layer 203.

25 In this embodiment, the water retaining layer 203

is 180 microns thick and the humidifying water inlet
202 is 100 microns thick. The porosity of the
humidifying water inlet 202 is 0.8 although the
porosity of the water retaining layer 203 is 0.9.

5   The water retaining layer holder 206 is equipped
with anode gas flow channels 302 and 307, cathode gas
flow channels 304 and 305, cooling water flow channels
303 and 306, and bolt holes 301.

Fig. 4 shows the surface of the unit cell
10   separator 104 for a unit cell 101 in the PEFC 100 over
which the anode gas flows. (This surface is called an
anode surface.) The anode gas is fed from the anode
gas flow channel 302, flows through the gas
distribution section 401 that is provided to
15   distribute the gas over the whole separator and then
through the gas flow channels 402 partitioned by gas
distribution ribs 403, and goes out from the anode gas
flow channel 307. The bolt holes 301 are used to
tighten the cell assembly with bolts. The cooling
20   water flow channels 303 and 306 in the top and bottom
centers of the cell separator 104 are used to flow
cooling water. The manifolds 304 and 305 in the end
are used to flow the cathode gas.

The unit cell separator 104 of FIG... 4 has its
25   rear surface over which the cathode gas flows. (This

surface is called a cathode surface.) The location of the manifolds 302 and 304 on the top and 305 and 307 on the bottom on the cathode surface are reverse to that of manifolds on the anode surface. The cathode

5 gas is fed from the cathode gas flow channel 304, flows through the gas distribution section and the gas flow channels, and goes out from the anode gas flow channel 305. The MEA 120 and the gas distribution layer 106 are sandwiched between this cathode surface

10 and the anode surface of the other unit cell separator as shown in Fig. 1. In this way, a unit cell 101 of Fig. 1 is constructed.

The humidifier 108 comprises a water permeable membrane 201, a water retaining layer 203, a

15 humidifying water inlet 202, a member for connecting the humidifier to the cell assembly, and a packing. This humidifier is connected to the cell assembly of the unit cell 101 with the water permeable membrane 201 interposed.

20 It is possible to provide one or more humidifiers 108 on the end(s) of a cell assembly or to provide the humidifier for each unit cell or for a set of unit cells. It is preferable, as in this embodiment, to provide the humidifier 108 on the upstream end of the

25 unit cell assembly 119 from which the anode gas is

supplied. This enables the use of a single humidifier to humidify the anode gas. Although this embodiment is not equipped with a humidifier for the anode gas as the cathode PEM 102 can humidify the gas fully with water generated by power generation, it is possible to provide a cathode gas humidifying means in the cathode gas flow channel. Further, as part of the cooling water is used as humidifying water, the generated heat can be used effectively without depriving excessive heat from the cell assembly.

When the humidifier is placed between two unit cells, the humidifier must be conductive to transfer electrons. Accordingly, parts that hold the water retaining layer and the water permeable membrane must also be conductive. The fuel cell assembly of this embodiment is named S1.

(Embodiment 2)

The water retaining layer 203 of this embodiment uses a non-woven cloth made of hydrophilic polyethylene and hydrophilic polypropylene prepared by substituting part or all of hydrogen atoms of polyethylene and polypropylene by fluorine atoms and sulphonating them. The sulfonic group must be of the proton type. The water retaining layer 203 is bonded to the water permeable membrane 201 with a small

amount of monomer that is an electrolyte of the water
permeable membrane 201 of Embodiment 1 therebetween as
the adhesive. The other components of this embodiment
such as unit cell separator 104, MEA 120, and gas
5   diffusion layer are the same as those of Embodiment 1.
The PEFC of Embodiment 2 is prepared in the similar
manner as Embodiment 1 as shown in Fig. 1. The fuel
cell assembly of this embodiment is named S2.

(Embodiment 3)

10   Referring to Fig. 5, the humidifying water inlet
202 at which the cooling water from the cooling water
flow channel 204 touches the water retaining layer is
replaced by a porous carbon filter 501 that has an
average micro-pore diameter of 50 microns and porosity
15   of 0.55. The cooling water is supplied to the water
retaining layer through this porous carbon filter 501.
This can omit the water permeable membrane 201 of
Embodiment 1 as the porous carbon filter 501 can
control the flow rate of part of the cooling water
20   from the cooling water flow channel to the water
retaining layer 203. In other words, this embodiment
can control the water content of the water retaining
layer by the porous carbon filter 501 and let the
water retaining layer directly humidify the gas even
25   when the water permeable membrane 201 is not provided.

We inventors tested the humidifying performance of
this embodiment using porous carbon filters of average
micro-pore diameters of 50, 75, 100, 150, and 200
microns and found that these porous carbon filters can
5   humidify fuel gases similarly.

The cell stack of this embodiment is prepared by
using a porous carbon filter of 100 microns in average
micro-pore diameter for the humidifier and the other
components which are the same as those of Embodiment 1.
10   The fuel cell assembly of this embodiment is named S3.

(Comparative example)

This embodiment uses a humidifier comprising a
water permeable membrane 201 only (excluding the water
retaining layer 203 of Fig. 2). The water permeable
15   membrane is the same as that 201 of Embodiment 1. The
humidifying water inlet 202 has ten 0.5 mm-diameter
holes to supply part of the cooling water to the
humidifier 108. The other configuration of this
example except the humidifier 108 is the same as that
20   of Embodiment 1. The fuel cell assembly of this
example is named R1.

Another example R2 is prepared having the same
configuration as the Example R1 except that the water
permeable membrane 201 uses a polytetrafluoroethylene
25   membrane of 0.05 micrometer in average micro-pore

diameter.

(Embodiment 4)

We inventors tested the fuel cell assemblies S1, S2, and S3 of Embodiments 1, 2, and 3 and the fuel cell assembly R1 of Comparative example R1 under conditions of:

supplying a mixture of 70%-by volume of hydrogen gas and 30%-by volume of carbon dioxide gas to the anode through the humidifier 108 to humidify thereof,

supplying air as the cathode gas to the unit cells 101 directly without humidifying thereof, and

keeping the unit cell temperature at 70°C and the inlet temperature of the cooling water at 60°C to initially supply hot water of 60°C to the humidifier 108, assuming that the outside air temperature is 25°C.

The conditions also contain that 70% of hydrogen and 40% of oxygen are used for power generation, that respective currents are fixed, and that the gases are supplied at normal pressures.

First, we supplied dry gases (having a dew point of -20°C) required to generate electricity of 0.5 mA/cm^2 to the cell assemblies without a load and measured the humidification rates of gases that passed the cell assemblies by a mirror-type dew-point hygrometer. The anode gases humidified by the

humidifiers of the cell assemblies S1, S2, and S3 without a load could have a dew point of 60 to 65°C, which is approximately equal to the cell temperature during power generation. Contrarily, the cell assembly

5   R1 of Comparative Example 1 could assure the dew point of 60 to 65°C but increased the pressure loss of the anode gas from 50 to 190 mmH_2O. It is known that this pressure loss is caused by a blockage of the anode gas flow channel due to the swelling of the membrane. The

10   cell assembly R2 of Comparative Example 2 clears this pressure loss problem but the dew point of the humidified anode gas is very low (25°C), which means insufficient humidification rate.

(Embodiment 5)

15   In succession to Embodiment 4, we carried out a continuous power generation test on each of cell assemblies S_1, S_2, and S_3 of Embodiments 1, 2, and 3 under the power generation test conditions of Embodiment 5. The current density in this running test

20   is 0.5 mA/cm^2.

The voltage drops of the cell assemblies S_1, S_2, and S3 were very small in continuous power generation. The mean voltage drops of cell assemblies S_1, S_2, and S3 are respectively 9, 12, and 13 mV (in that order)

25   after power generation of 1000 hours.

On the contrary, the cell assembly R_1 of
Comparative Example 1 increased the pressure loss of
the anode gas from 50 to 190 mmH$_2$O and the mean voltage
drop to 120 mV after power generation of 1000 hours.

5   Further, the mean voltage drop of the cell assembly R2
of Comparative Example 2 was very great (450 mV) after
power generation of 1000 hours as the gas
humidification was insufficient.

(Embodiment 6)

10   We kept the cell assemblies S_1, S_2, and S_3 in a
temperature-controlled room whose temperature could be
kept at -5°C and 25°C and carried out a continuous
power generation test on them. The test conditions
were: continuous power generation at a room

15   temperature of 25°C for 14 hours, current density of
0.2 mA/cm^2, hydrogen use ratio of 70%, and oxygen use
ratio of 40%. After this test cycle is completed, we
cooled the test room including the cell assemblies
from 25°C to -10°C in 2 hours with each cell assembly

20   filled with the anode gas and the cathode gas and
without any gas flow. In this case, each cell assembly
has no loaded and stops power generation. After the
room temperature reaches -5°C, we kept the test room at
-5°C for 6 hours, increased the room temperature again

25   to 25°C in 2 hours, and started the second test cycle.

We repeated this test cycle (comprising the steps of power generation, cooling, leaving still, and warming) once a day for 30 days.

After this temperature cycle test was completed,
5   we carried out a power generation test on the cell assemblies under the conditions of Embodiment 5. As the result of this temperature cycle test, we know that the cell assemblies of Embodiments 1, 2, and 3 have their performances reduced little and the voltage
10   drops are only 20 to 30 mV after the temperature cycle test. Contrarily, the cell assemblies of Comparative Examples 1 and 2 have great voltage drops (250 to 310 mV). When disassembling the tested cell assemblies, we detected some breaks on the membrane of the humidifier.
15   We assumed that these membrane breaks were caused by freezing of excessive water in the humidifier. Additionally, we detected no break in humidifier membranes of cell assemblies S1, S2, and S3 after disassembling.

20   (Embodiment 7)

When the water retaining layer 203 having a mean micro-pore diameter in Embodiment 1 is hydrophilic, the water retaining layer can solely humidify the anode gas even without the water permeable membrane
25   201. In other words, it is possible to humidify the

anode gas by causing the water retaining layer 203 to hold part of water supplied to the cell or water that is supplied directly from the outside and causing the wet water retaining layer 203 to directly touch the anode gas.

This has the following merits: simplified humidifying mechanism without the water permeable membrane 201, Increase of humidification rate due to provision of no water permeable membrane 201, and arbitrary shape and disposition off the water retaining layer 203. Preferred materials available to the water retaining layer 203 can be hydrophilic porous materials prepared by making polytetrafluoroethylene, polystyrene or copolymer of styrene and butadiene hydrophilic. The humidification rate can be controlled by changing the contact area between the water retaining layer 203 and the anode gas.

The cell assembly S7 of Embodiment 7 is prepared in the same configuration as that of Embodiment 1 except that the water permeable membrane 201 is not provided. We tested this cell assembly S7 under conditions of supplying a mixture of 70%-by volume of hydrogen gas and 30%-by volume of carbon dioxide gas to the anode through the humidifier of this invention

to humidify thereof, supplying air as the cathode gas to the unit cells 101 directly without humidifying thereof, and keeping the unit cell temperature at 70°C and the inlet temperature of the cooling water at 60°C

5 to initially supply hot water of 60°C to the humidifier 108 of Fig. 1, assuming that the outside air temperature is 25°C.

The conditions also contain that 70% of hydrogen and 40% of oxygen are used for power generation, that

10 respective currents are fixed, and that the gases are supplied at normal pressures.

First, we supplied dry gases (having a dew point of -20°C) required to generate electricity of 0.5 mA/cm^2 to the cell assemblies without a load and

15 measured the humidification rates of gases that passed the cell assemblies by a mirror-type dew-point hygrometer. The anode gases humidified by the humidifiers of the cell assemblies S_1, S_2, and S_3 without a load could have a dew point of 65 to 67°C,

20 which is approximately equal to the cell temperature during power generation. When compared by the cell assembly S_1 of Embodiment 1, the cell assembly S7 can humidify the anode gas directly by the water retaining layer as the water permeable membrane is not provided

25 and consequently increase the humidification rate of

the anode gas. In other words, the water retaining layer of the cell assembly S_7 can be smaller when the humidification rate is fixed. Consequently, this is effective in making the fuel cell assembly compact.

5   (Embodiment 8)

When the humidifier employs the water permeable membrane 201, the anode gas leaks towards the water while diffusing in the water permeable membrane 201 and prevents the humidifying water from transferring

10   into the water permeable membrane. To solve this problem, a method is provided to eliminate the anode gas that diffuses in the water permeable membrane 201.

This method utilizes a fact that the micro-pore diameter of the porous material of the water retaining

15   layer 203 is much greater than that of the water permeable membrane 201. In other words, as it is very easy to disperse metal catalyst or metal oxide catalyst in micro-pores of the water retaining layer 203, a catalyst having a function of oxidizing

20   hydrogen three-dimensionally is dispersed in the water retaining layer 203. This structure has the merits below. For example, the water permeable membrane 201 becomes wet and dry repeatedly by the anode gas as the PEFC starts and stops. So, when provided on the

25   surface of the water permeable membrane 201, the

catalyst layer will break or separate from the water

permeable membrane by shrinking and swelling of the

water permeable membrane 201 and gradually loses the

function of oxidizing hydrogen. Contrarily, when the

5   cell assembly uses the water retaining layer 203

having catalyst dispersed in it, the catalyst will be

rarely deteriorated because the water retaining layer

203 itself is not in direct contact with the gas and

rarely affected by the water content as the PEFC

10   starts and stops. Further, the catalyst can be easily

dispersed in the porous material that constitutes the

water retaining layer 203 at a low cost as the porous

material has a great micro-pore diameter. Furthermore,

the catalyst dispersed in the water retaining layer

15   can oxidize hydrogen dissolved in water more quickly

and efficiently than the catalyst layer attached to

the surface of the water permeable membrane 201.

Fine platinum particles, carbon particles on which

platinum particles are dispersed, and titanium oxide

20   are available as the catalyst. Any catalyst is

available as long as it has a function to oxidize

hydrogen. There are various methods of dispersing

these catalyst in the water retaining layer 203: a

method of directly impregnate the water retaining

25   layer 203 with catalyst particles and a method of

depositing metal particles in the water retaining

layer by a sol-gel reaction such as the alcoxide

method or by adding a reducing agent such as

formaldehyde, hydrazine, or hydrogen peroxide.

5   Referring to Fig. 2, we prepared a catalyst-

dispersed water retaining layer by dipping the water

retaining layer in a catalyst-suspended alcohol liquid

which suspends platinum-plated graphite particles

(mean grain size of 0.1 micrometer) in alcohol such as

10   ethanol, vacuum-dried thereof, and secured it by the

water retaining layer holder. We prepared a fuel cell

assembly S_8 using this water retaining layer and the

water permeable membrane in the manner similar to

Embodiment 1.

15   We tested the humidification of the anode gas of

the cell assembly S_8 under the conditions similar to

those of Embodiment 1 and found that the humidified

gas had a dew point of 65 to 67°C. Therefore it is

apparent that the water retaining layer of this

20   embodiment has no influence on humidification of the

anode gas. Further, the water retaining layer of this

embodiment can facilitate provision of a mechanism to

oxidize hydrogen that passes through the water

permeable membrane and remove it as water by a simple

25   method. After the power generation test, we measured

the quantity of hydrogen left in the cell assembly by substituting hydrogen gas in the cell assembly by nitrogen gas using the anode gas port 110 and the cathode gas port 112 of the cell assembly (Fig. 1),

5   closing one of the cooling water ports, sucking the gas from the other cooling water port, and measuring the quantity of hydrogen gas in the sucked gas by a gas chromatography or the like. We found that there was no remaining hydrogen gas in the sucked gas. This

10   means that the water retaining layer of this embodiment can completely oxidize hydrogen that passes trough the water permeable membrane.

       (Embodiment 9)

       FIG... 6 shows a schematic diagram of a power

15   generation system having a PEFC of this invention.

       The natural gas (containing hydrogen) 601 to be supplied to the anode is obtained by reforming the natural gas (sent from the pump 608) with steam by the reformer 603 and contains hydrogen gas of 30 to 80% by

20   volume. The reformer 603 contains a catalyst having a function that selectively oxidizes a small amount of carbon monoxide (CO) to prevent a voltage drop of the fuel cell assembly 612. If the raw gas (natural gas) contains any harmful impurity (such as sulfur and the

25   like) that deteriorates the function of the catalyst

in the reformer 603, an impurity remover 613 must be
provided in the upstream side of the reformer 603. The
hydrogen gas that is left unreacted in the anode gas
is returned to the reformed through the anode gas
5   exhaust pipe 614.

Air 602 as a cathode gas is supplied to the fuel
cell assembly 612 by the pump 609. The reacted cathode
gas is exhausted from the fuel cell assembly 612
through the cathode gas exhaust pipe 616.

10   Distilled water 606 as the humidifying water is
supplied to the fuel cell assembly 612 by the pump.
This embodiment uses an identical pipe to supply the
humidifying water and the cooling water. In the cell
assembly 605 comprising separators, membranes, and
15   electrodes, the humidifying water is sent to the
humidifying section 604 (equivalent to 108 of FIG...
1) and the cooling water is sent to the cooling water
separator 107 of Fig. 2. The cooling water deprives
the cell assembly of the reaction heat, becomes hot,
20   and transfers the heat to the water in the hot water
tank 607 by the heat exchange 611. The circulation
pump 610 circulates water forcibly.

Besides the water supplying method of this
embodiment, it is possible to supply the humidifying
25   water by another pump to supply it independently of

the cooling water.

The fuel cell assembly of this system generates a direct current power. It is also possible to provide an inverter circuit to turn direct current to

5   alternate current for home use. Further, this fuel cell assembly can be used for the other applications, for example, as a power supply for electric automobiles. In this application, the reformer 603 can be substituted by a hydrogen container, a hydrogen

10   storing apparatus, or the like. The hot water tank 607 can be omitted and the heat exchange 611 for exchanging heat with the water in the hot water tank 607 can be replaced by an air-cooler for simple and easy heat exchange.

15   The fuel cell assembly of this invention can humidify the fuel gas, keeping a low pressure loss of the fuel gas.